

collision cell to generate daughter spectra from selected parent ions. Samples were introduced into the source by the direct chemical ionization method (12). Isobutane and, independently, isobutane together with NH_3 , were employed as the chemical ionization reagent gases (0.4-0.7 torr), and argon was used as the collision gas at a gauge pressure of 2.0 mtorr. The collision energy was 20 eV. Characteristic parent and daughter ions were observed and recorded as follows; mescaline: m/z 212 ($\text{M}+\text{H}$)⁺, 195 ($\text{M}+\text{H}-\text{NH}_3$)⁺, 180 ($\text{M}+\text{H}-\text{NH}_3-\text{CH}_3$)⁺, 168 ($\text{M}+\text{H}$ -side chain)⁺, 165 ($\text{M}+\text{H}-\text{NH}_3-\text{CH}_2\text{O}$)⁺; 3,4-dimethoxy- β -phenethylamine: m/z 182 ($\text{M}+\text{H}$)⁺, 165 ($\text{M}+\text{H}-\text{NH}_3$)⁺, 150 ($\text{M}+\text{H}-\text{NH}_3-\text{CH}_3$)⁺, 138 ($\text{M}+\text{H}$ -side chain)⁺; 3,5-dimethoxy-4-hydroxy- β -phenethylamine: m/z 198 ($\text{M}+\text{H}$)⁺, 181 ($\text{M}+\text{H}-\text{NH}_3$)⁺, 166 ($\text{M}+\text{H}-\text{NH}_3-\text{CH}_3$), 153 ($\text{M}+\text{H}$ -side chain-H)⁺, 121 ($\text{M}+\text{H}-\text{NH}_3-2\text{CH}_2\text{O}$)⁺. The daughter spectra recorded with NH_3 reagent gas did not display the peak due to loss of the side chain but were otherwise very similar to those recorded using isobutane.

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FLAVONOIDS FROM *STEPHANODORIA TOMENTELLA*

NIANBAI FANG,¹ MARK LEIDIG, and TOM J. MABRY

The Department of Botany, The University of Texas at Austin, Austin, Texas 78713

In a continuation of our chemotaxonomic studies of the '*Gutierrezia-Xanthocephalum* complex' (tribe Astereae, Compositae) (1-6), we have now investigated *Stephanadoria tomentella* Greene. This taxon is a monotypic genus at one time thought to be related to *Gutierrezia* and *Xanthocephalum*. In this study we report eight flavonoids, namely: kaempferol 3-O- β -glucoside, kaempferol 3-O- β -galactoside, kaempferol 3-O- β -glucuronide, quercetin 3-O- β -glucuronide, quercetin 3-O- β -glucoside, vitexin, vicenin-2, and quercetin 3-methyl ether. We also include previously unreported uv data for the natural product kaempferol 3-O- β -glucuronide and ¹H-nmr data for its trimethylsilyl ether.

EXPERIMENTAL

PLANT MATERIAL.—Leaves and heads of *S. tomentella* (500 g) were collected from the state of San Luis Potosi, Mexico, near the railroad station at Gerritos between Hwy. 57 and Hwy. 80 by Mark Leidig and Meredith Lane in June 1981. A voucher specimen (Mark, S.N.) is on deposit in the Plant Resources Center at the University of Texas at Austin, Austin, Texas.

¹Permanent address: The Hubei College of Chinese Traditional Medicine, Wuhan, China.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Dried material (500 g) was extracted sequentially with 85% and 50% aqueous MeOH. After filtration the extracts were combined and concentrated in vacuo. The aqueous syrup was partitioned first against CH₂Cl₂ and then EtOAc. The CH₂Cl₂ extract was concentrated and adsorbed onto Polyclar (Polycar AT, GAF Corp.). After drying, the resulting powder was charged onto a Polyclar column packed in H₂O-MeOEt-MeOH-Me₂CO (13:3:3:1). Flavonoids were eluted with the same solvent system. The EtOAc extract was chromatographed over a Polyclar column using the same procedure described for the CH₂Cl₂ extract. For both columns, fractions were collected on the basis of monitoring the bands with uv light. All bands were further separated by paper chromatography (Whatman 3MM) using 15% HOAc and TBA (t-BuOH-HOAc-H₂O, 3:1:1). Final purification of each compound for spectral analysis was by standard procedures (7) using 80% or 100% MeOH over Sephadex LH-20 columns. Compounds were identified by uv, ¹H nmr, ms (following acid hydrolysis for the glycosides), color reactions (7) and authentic sample comparisons. Previously unreported data for kaempferol 3-O-β-glucuronide: uv λ max (MeOH) 265, 300sh, 350; λ max (MeOH+NaOMe) 271, 330sh, 397; λ max (MeOH+AlCl₃) 268, 305sh, 375; λ max (MeOH+AlCl₃/HCl) 267, 300, 355, 400sh; λ max (MeOH+NaOAc) 369, 325sh, 378; λ max (MeOH+NaOAc/H₃BO₃) 261, 300sh, 372; ¹H nmr (as trimethylsilyl ether, CCl₄, TMS) δ 3.40-3.80 (4H, m), 5.67 (1H, m), 6.12 (1H, d, J=2.5 Hz), 6.23 (1H, d, J=2.5 Hz), 6.83 (2H, d, J=8.5 Hz), 7.93 (2H, d, J=8.5 Hz).

Details of identification are available upon request to the senior author.

TRIMETHYLSILYLATION.—This was performed as described by Mabry *et al.* (7).

HYDROLYSIS.—Hydrolysis of the glycosides with 0.1 N TFA (45 minutes) yielded the expected aglycones and sugar residues except for kaempferol 3-O-β-glucuronide. The hydrolysis of kaempferol 3-O-β-glucuronide was carried out by both β-glucuronidase and 1 N HCl (1 h).

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FLAVONOID AGLYCONES FROM *AGERATINA TOMENTELLA*

NIANBAI FANG¹ and TOM J. MABRY

The Department of Botany, The University of Texas at Austin, Austin, Texas 78713

As a part of our chemosystematic survey of the tribe Eupatorieae (Compositae) (1-4), we investigated the flavonoid aglycones of *Ageratina tomentella* (Schard.) R.M. King & H. Robinson. Six 6-methoxyflavones were isolated, namely: 6-methoxyluteolin and its 3'-methyl ether, 7,3'-dimethyl ether, 7,4'-dimethyl ether, and 7,3',4'-trimethyl ether, and 6-methoxyapigenin. The 6-methoxylation, 7-methoxylation, and 6,7-dimethoxylation appear to be characteristic of the main evolutionary line in the genus *Ageratina* (3-6). However, other *Ageratina* species produce flavonols alone or mixed with flavones (3-6).

¹Permanent address: The Hubei College of Chinese Traditional Medicine, Wuhan, People's Republic of China.